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NUCLEAR OXIDATION IN THE FLAVONES AND RELATED COMPOUNDS

Part XIII. A Discussion of the Results

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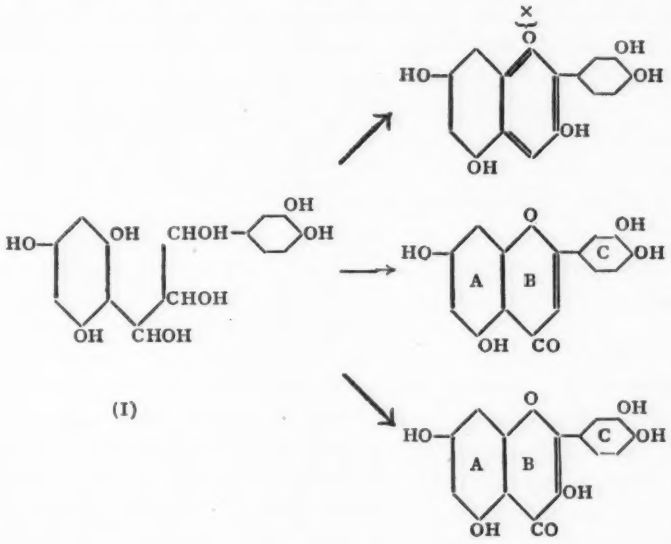
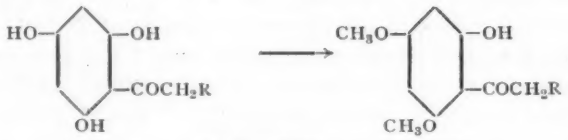
Received April 29, 1948

I. Biogenesis

In a paper by Rao and Seshadri[1] published in 1943 data bearing on the occurrence of anthoxanthins and their association in nature were presented and discussed. They were found to support the theory of Robinson regarding the origin of anthocyanins and anthoxanthins from a common precursor (I). The most outstanding structural feature of the anthoxanthins is the large number of states of oxidation in which ring (A) is capable of existing. The biological data could satisfactorily be explained on the basis that flavones and flavonols having two hydroxyl groups (5: 7) in ring (A) represent primary stages in biogenesis and those having three hydroxyls (5: 6: 7 or 5: 7 : 8) and four hydroxyls (5: 6: 7: 8) involve additional stages of oxidation.

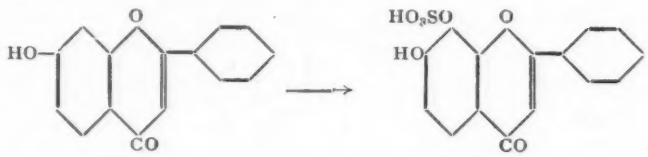


Laboratory experiments on nuclear oxidation in support of the above conclusions could not be carried out at that time owing to severe war conditions. They could be taken up more recently and the subject examined in detail. At the beginning it appeared that direct attack on the flavones themselves was not likely to be successful in view of the failures recorded in the past.[2, 7] Consequently as the first stage in the development of the model experiments phloroglucinol derivatives were chosen. Phloroacetophenone and ω-methoxy-phloroacetophenone (II) and their derivatives had not been subjected to nuclear oxidation before. In order to prevent general oxidation of the molecules the 4 : 6-dimethyl ethers (III) were prepared leaving the hydroxyl in the 2-position alone free. The partial methylation is easily effected since this particular hydroxyl is definitely more resistant to methylation than the others.



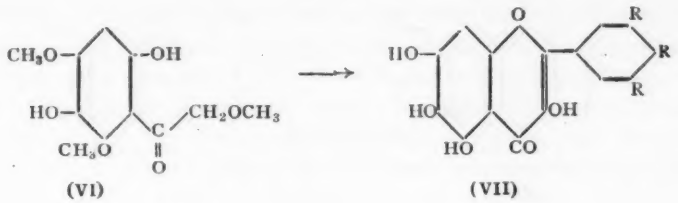
(II) R=H or OCH_3 (III)

As the most suitable and direct oxidising agent alkaline potassium persulphate was chosen. It behaves as a kationoid (electrophilic) reagent and introduces a hydroxyl group in the position para to the activating group; ortho substitution is also possible as a second alternative though not so readily, if a para position is not available. As a convenient intermediate stage a sulphate ester is formed and this being soluble in water, separation of the unchanged original substance becomes easy. Subsequent hydrolysis of the ester yields the final product. In the course of our work on nuclear oxidation this intermediate sulphate could be isolated in one case[3] as a crystalline solid and characterised.

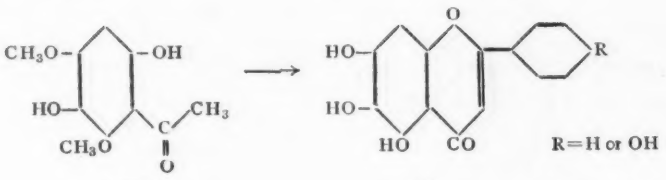


(IV) (V)

The oxidation products (VIII, VI) of phloroacetophenone and its ω-methoxy-derivative could then be subjected to the flavone condensation; thus all the four flavonols (VII) of the quercetagetin series[4] (1) 6-hydroxy-galangin, (2) nor-tangeretin, (3) quercetagetin and (4) 6-hydroxy myricetin were synthesised and so also the flavones (IX), baicalein and scutellarein.[5]

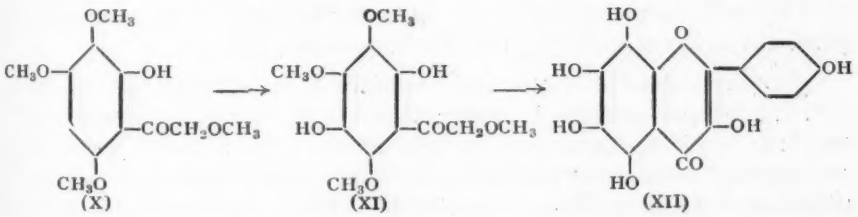


(VI) (VII)



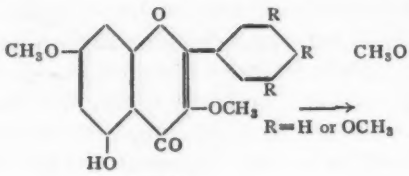
(VIII) (IX)

As the next higher stage, starting with gossypetol-tetramethyl-ether the flavonols of the calycopteretin series[6] could be similarly synthesised.

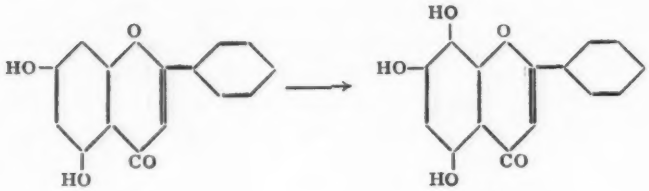


(X) (XI) (XII)

More recently the nuclear oxidation of typical 5: 7-hydroxy flavones and flavonols could be effected. Though attempts made by earlier workers[2] had been unsuccessful the reaction was reinvestigated[7] repeatedly since the possibility of such nuclear oxidation in the flavone series was so definitely indicated by evidences from other directions. Here too partial methylation had to be first done in order to protect against general oxidation. It was found to be quite easy to carry this out leaving the resistant 5-hydroxyl alone free. Alkaline persulphate proved again to be the most satisfactory oxidising agent. At first there was difficulty owing to the very sparing solubility of these 5-hydroxy compounds in aqueous alkali. This was subsequently got over by adding the required amount of pyridine in order to get a clear solution. Thus starting from the flavonols of the quercetin series have been synthesised in an easy manner the flavonols (XIV) of the gossypetin series[7]—8-hydroxy-galangin, herbacetin, gossypetin and hibiscetin—and the flavone (XVI), nor-wogonin[8] from chrysin.



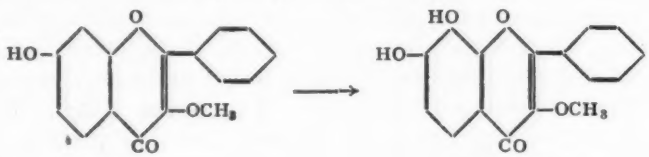
(XIII) (XIV)



(XV) (XVI)

Later it was realised that it was not invariably necessary to protect the hydroxyl group in the 7-position. As a matter of fact it was an advantage to have it free in some cases since the compound was then soluble in aqueous alkali and gave rise to better yields of the oxidation product.

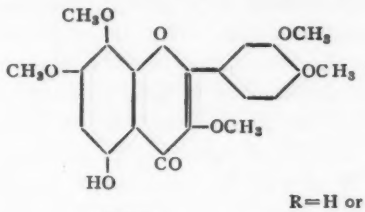
As shown above it is very easy to oxidise a 5: 7-hydroxy flavone into a 5: 7: 8-hydroxy compound. There seemed to be no chance of preparing the 5: 6: 7-hydroxy compounds by this means. The hydroxyl group in the 5-position activates markedly the 8-position. The simplest case is the oxidation of 5-hydroxy flavone to primetin.[9] When the 8-position is occupied as in gossypetin 3: 7: 8: 3′: 4′-pentamethyl ether[10] (XIX) no reaction takes place and the compound is recovered unchanged. As far as the hydroxyl in the 7-position is concerned it is generally known to activate position 8 in all reactions. The nuclear oxidation is no exception to this. Actually in some cases good yields of 7: 8-hydroxy compounds[3] (XVIII) could be obtained from 7-hydroxy compounds (XVII).



(XVII) (XVIII)

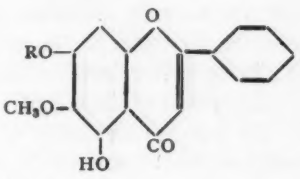
Since the free 6-position was found to be unreactive in gossypetin-pentamethyl ether (XIX), the 5: 7: 8-hydroxy flavones and flavonols cannot be used for obtaining the tetrahydroxy (5: 6: 7: 8) compounds (XII). On the other hand it is quite easy to oxidise the 5: 6-7-hydroxy compounds

to the 5:6:7:8-hydroxy analogues employing the conditions already mentioned. In these cases it appeared to be necessary to protect even the 7-hydroxyl, since oroxylin-A (XX, R = H) did not give satisfactory results whereas baicalein 6:7-dimethyl ether (XX, R = CH_3) underwent the change smoothly.[11] From nortangeretin, calycopeteretin and from quercetagetin, 6:8-dihydroxy quercetin have been prepared[10] (XXI →XXII).

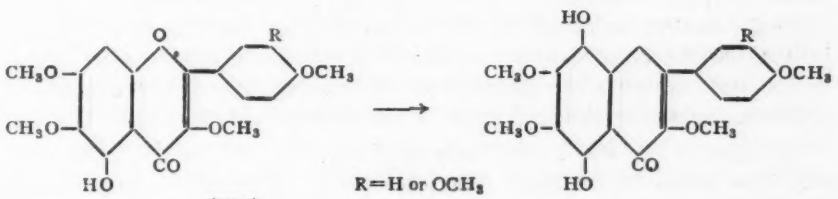


(XIX)

R=H or CH_3



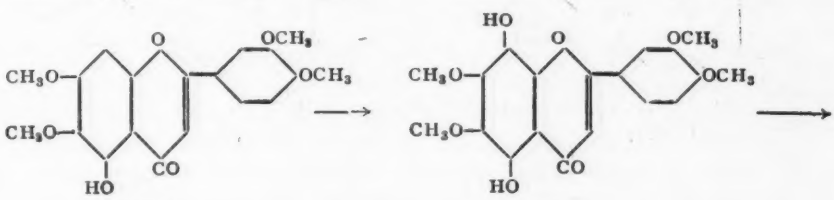
(XX)



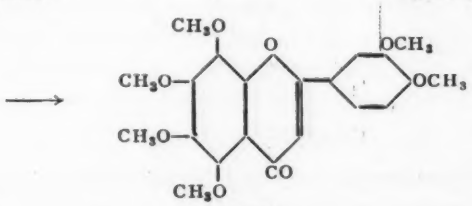
(XXI)

R=H or OCH_3

Similarly the synthesis has been carried through using the flavones, baicalein, scutellarein and 6-hydroxy-luteolin (XXIII) and members of the nobiletin (XXV) (nornobiletin) series obtained.[11, 12]

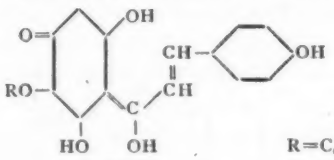


(XXIII) (XXIV)



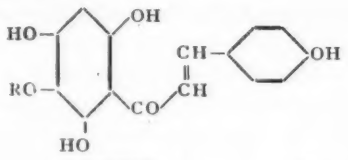
(XXV)

The experimental results described so far would lead to the following conclusions regarding the evolution in nature of compounds with three and four hydroxyl groups in ring (A). (1) 5: 7-Hydroxy-flavones and flavonols as well as their analogues with ring (B) open are involved in the oxidation. Partial protection of the hydroxyl groups is effected whatever may be the mechanism adopted. (2) 5: 7: 8-Hydroxy-flavones and flavonols (gossypetin and norwogonin series) result from the corresponding 5: 7-hydroxy-flavones and flavonols by nuclear oxidation in the 8-position. This takes place very readily in the laboratory. Though the alternative, that is, the nuclear oxidation of the open form and subsequent ring closure to yield this type could not be altogether excluded, it seems to be unlikely as will be discussed below. (3) For the formation of the 5: 6: 7-hydroxy-flavones and flavonols the oxidation should involve the open form and the ring closure should take place subsequently. It has already been mentioned that these compounds cannot be produced from the fully formed 5: 7-hydroxy-flavones themselves since the nuclear oxidation of the 6-position does not take place particularly when the 8-position is unsubstituted. As satisfactory model experiments could be taken the oxidation of phloroacetophenone and ω-methoxy-phloroacetophenone-dimethyl ethers already described (III $\rightarrow$ VIII). Among compounds more closely related to flavones and with the ring (B) open, chalkones could be taken for experimentation. These occur in nature and examples with the ring (A) containing four and five hydroxyl groups (free or methylated) are found in carthamin[13] (XXVI) and *iso*-carthamin (XXVII) and pedicin, pedicellin (XXVIII) and their allies.[14, 15]

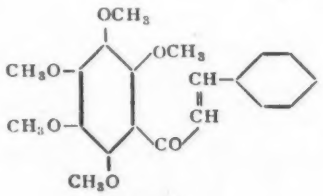


(XXVI)

R=$C_6H_{11}O_5$



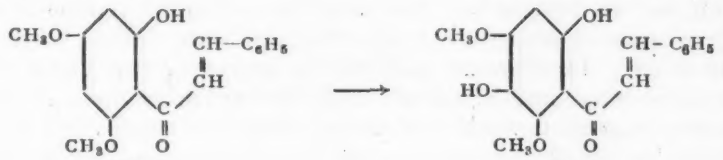
(XXVII)



(XXVIII)

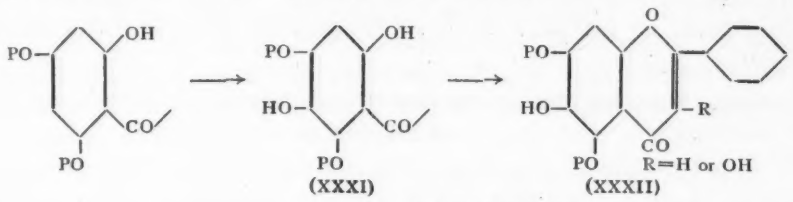
Experiments have now been carried out using 2-hydroxy-4-methoxy-chalkone and 2-hydroxy-4: 6-dimethoxy chalkone[16] (XXIX). They give rise to the

5-hydroxy compounds (XXX) under almost the same conditions as the simpler ketones.



(XXIX) (XXX)

Here it may be contended that in the plant after the oxidation of the open structure, ring closure could take place in either of two ways leading to the 5:6:7-hydroxy compounds or the 5:7:8-hydroxy compounds. The latter possibility seems to be very small from the following considerations. In laboratory experiments the 5:6:7-hydroxy flavones have greater stability and are formed in preference; in several cases 5:7:8-hydroxy flavones undergo isomeric change into the 5:6:7-type when boiled with hydriodic acid (see for discussion Sastri and Seshadri[5, 17]). Further, since some kind of protection of the hydroxyl groups is employed as indicated below, the ring closure to the 5:6:7-hydroxy form (XXXII) will be the most direct.



(XXXI) (XXXII)

P=Protecting group

(4) The 5:6:7:8-hydroxy-flavones and flavonols are produced by the nuclear oxidation of the corresponding 5:6:7-hydroxy compounds. This has been found to take place easily in the laboratory.[10, 11, 12] The occurrence of tangeretin and nobiletin in the closely related species of citrus nobilis has been mentioned in this connection. The alternative formation from the oxidation of the appropriate open form analogous to gossypetol-tetramethyl ether[6] (X) cannot be excluded though this process may be less direct. Actually pedicin, pedicellin and its associates are the results of such complete hydroxylation in the chalkone group (see Rao and Seshadri[15]). The case of pedicin and related compounds is discussed in detail later on.

II. Partial Protection

The necessity for the protection of the large number of hydroxyl groups in order to escape general oxidation has now to be emphasised. This also

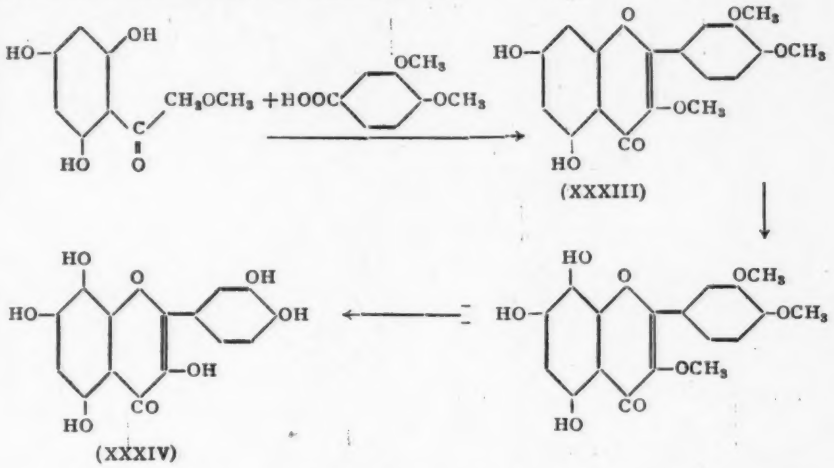
seems to direct the course of the nuclear oxidation. In the laboratory partial methylation can be conveniently adopted. Benzyl groups can also be used for this purpose and their more easy removability renders them handy in special cases though benzyl ethers are more difficult to prepare and to oxidise. In nature too protection of hydroxyl groups should be in operation whatever may be the protective mechanism involved. Probably the simplest suggestion would be that the protection is effected by a process of absorption or chemisorption on the enzymes required for biological oxidation. Such a mechanism has been suggested by Cook[18] in connection with the hydroxylation of carcinogenic hydrocarbons in the animal body.

In the case of the flavones and flavonols the 5-hydroxyl is definitely more resistant than the others and hence is left conveniently out during partial protection. It is then free to activate the 8-position giving rise to the easy formation of the 5:7:8-hydroxy compounds. Regarding the related open forms (*e.g.*, chalkones) it is again interesting to note that only one orthohydroxyl is resistant to methylation or protection[4, 5] (see also Robertson, Robinson and Struthers[19] for explanation) and partial protection can therefore be conveniently provided leaving out this hydroxyl which can then activate the available para position. Hence the schemes given above based on partial protection of the phenolic hydroxyl groups become valid.

III. Simplification of the Synthesis of Naturally Occurring Flavones

It is not infrequent that efforts to understand the methods of Nature lead to considerable simplification of laboratory methods of synthesis. The classical example of Robinson's synthesis of tropinone is well known. As a result of the experiments on nuclear oxidation a large number of naturally occurring flavones and flavonols have now been synthesised by methods which are direct and simple and mean considerable improvement over older methods. The new syntheses of the flavonols of the quercetagetin series[4] and of baicalein and scutellarein[5] have already been mentioned. These involve the oxidation of the partial methyl ethers of phloroacetophenone and ω-methoxy phloroacetophenone. Nuclear oxidation of the flavones themselves have led to more important results. Thus gossypetin, herbacetin and hibiscetin[7] are readily prepared from quercetin, kaempferol and myricetin. From the point of view of total synthesis the discovery that partial methyl ethers (XXXIII) with both 5 and 7-hydroxyl groups free, undergo oxidation more readily than the 5-hydroxy compounds is a definite advance, because these dihydroxy-compounds are the immediate products of Allan-Robinson

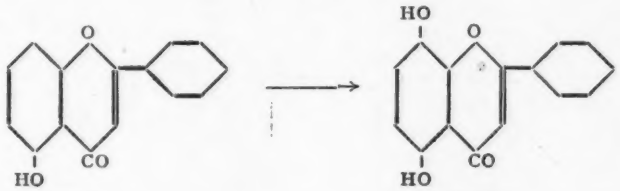
synthesis. The following illustration takes the case of gossypetin (XXXIV) synthesised from quercetin trimethyl ether.



(XXXIII)

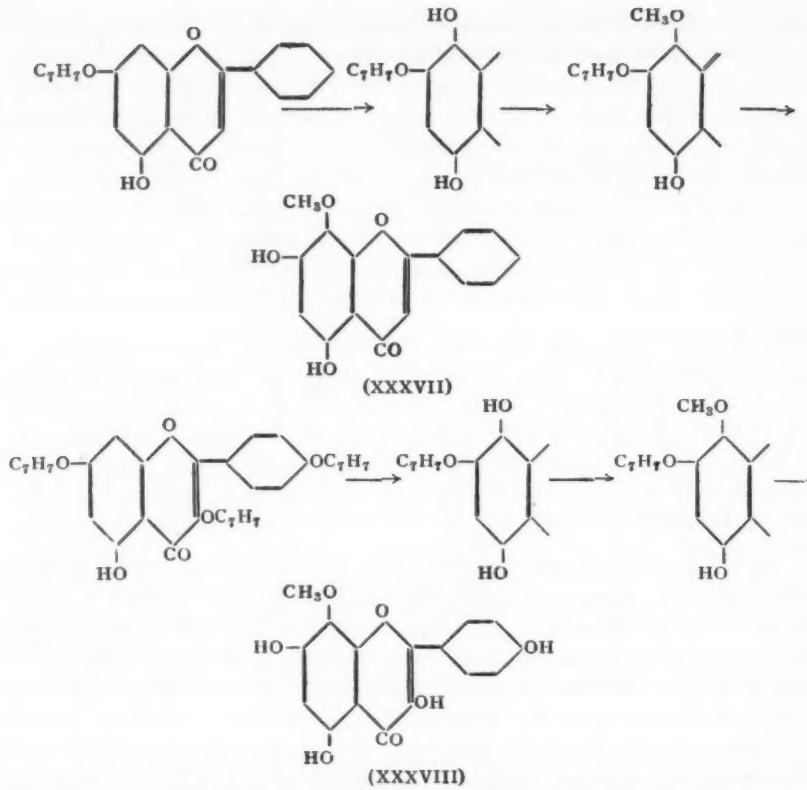
(XXXIV)

More complex examples are the synthesis of calycopteretin and its higher analogue[10] from nortangertin and quercetagetin and of nobiletin[12] and its group[11] from the flavones of the baicalein series. Norwogonin and primetin are simpler compounds, but there was originally considerable difficulty in their synthesis. Besides the usual difficulties of the preparation of flavones as compared with flavonols, such as poor yields and 3-acylation, in these cases there was the additional difficulty arising from isomeric change during demethylation. However nuclear oxidation of chrysin (XV) and 5-hydroxy flavone (XXXV) takes place smoothly and norwogonin[8] (XVI) and primetin[9] (XXXVI) can be obtained pure with great ease.



(XXXV) (XXXVI)

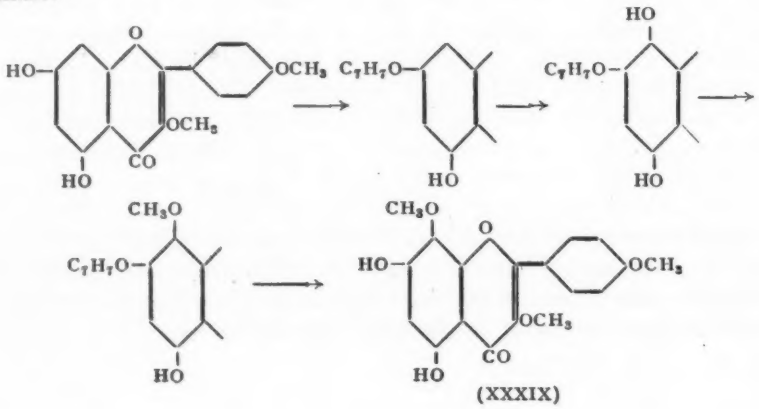
Another interesting application of nuclear oxidation is in the synthesis of the partial methyl ethers, wogonin[20] (XXXVII) and tambuletin[21] (XXXVIII). These involve initial protection of some hydroxyl groups by benzylation and removal of the benzyl groups finally.



(XXXVII)

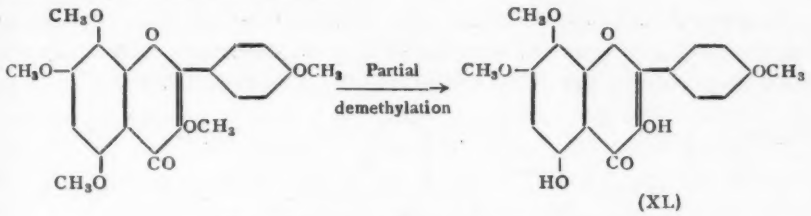
(XXXVIII)

Tambulin was originally considered to be 3:8:4′-trimethyl ether of herbacetin (XXXIX). This partial ether was prepared in the following manner.[22]



(XXXIX)

The product was however found to be different from tambulin. Examining other possibilities it has been shown that it should have the constitution of 7:8:4′-trimethyl ether of herbacetin (XL).[23] This ether is conveniently prepared by the partial demethylation of pentamethyl herbacetin using aluminium chloride.

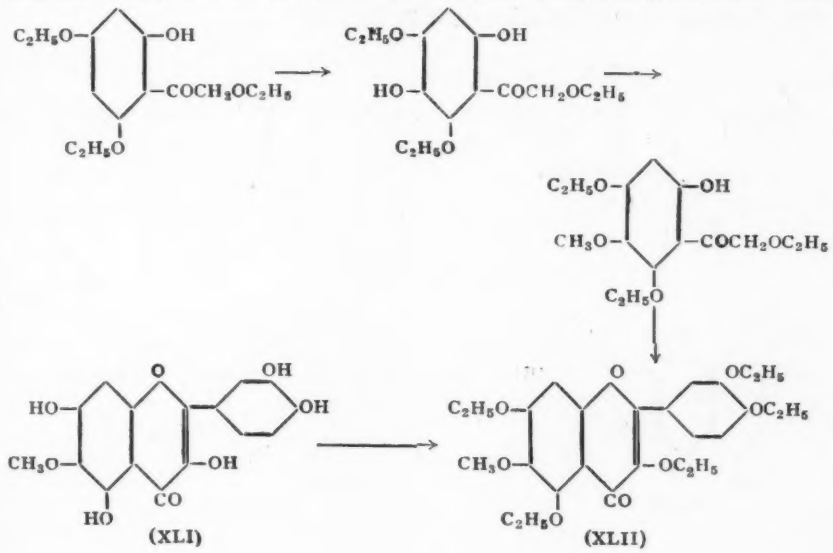


(XL)

IV. Study of Chemical Constitution

The method of nuclear oxidation is particularly useful in the study of the chemical constitution of glycosides and partial methyl ethers of anthoxanthins having three and four hydroxyls in ring (A). It has been successfully applied to a number of cases and has resulted in considerable simplification of the work and definiteness of the conclusions.

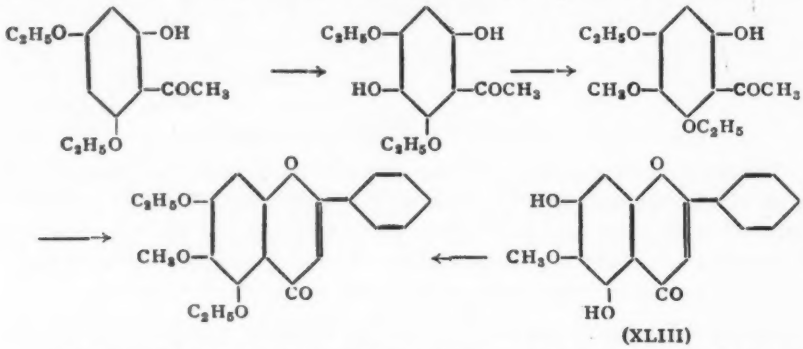
(*a*) *Partial methyl ethers.*—The earliest example was patuletin (XLI). That it is the 6-methyl ether of quercetagetin[24] was surmised from a comparison of its colour reactions with those of suitably chosen related compounds. This was then confirmed[25] by the preparation of pentaethyl patuletin (XLII) and its synthesis from ω-ethoxy phloroacetophenone. The



(XLI) (XLII)

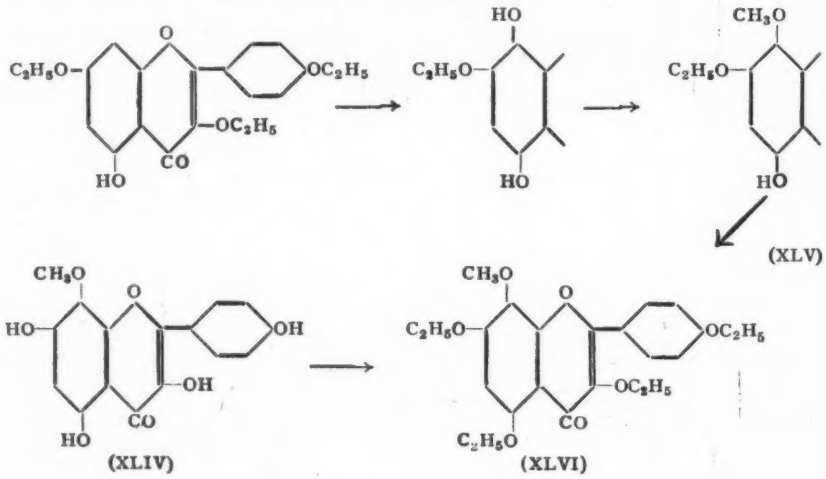
use of ethylation for this purpose and the study of the mixed ethers is a marked improvement in this type of work. The presence of free hydroxyl groups in these partial ethers is a disadvantage in both degradation and synthetic work. The difficulty is removed by ethylation and hence it has been adopted regularly in this laboratory.

Oroxylin-A (XLIII)is a similar case. It is the 6-methyl ether of baicalein and its constitution was also established in an analogous manner by the synthesis of its diethyl ether starting from phloroacetophenone.[26]



(XLIII)

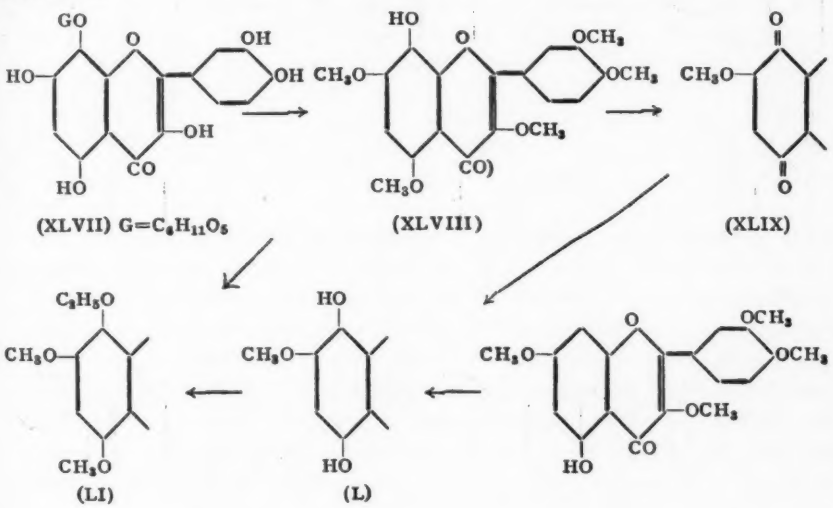
An example where the nuclear oxidation of a flavone itself has been employed is that of tambuletin[27] (XLIV). Its constitution as the 8-methyl-ether of herbacetin was inferred from its properties and colour reactions. This was confirmed by the preparation of its triethyl (XLV) and tetraethyl (XLVI) ethers and their synthesis[28] as follows:



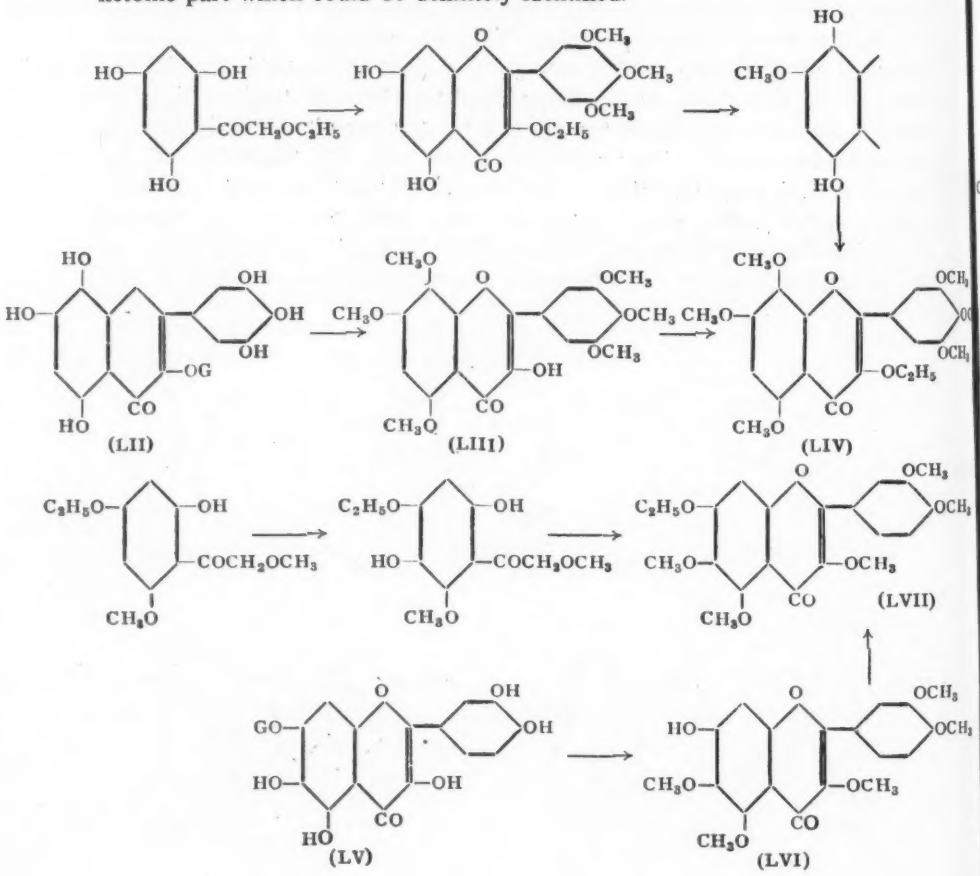
(XLIV) (XLV) (XLVI)

Later tambuletin itself was synthesised as already mentioned. This technique of nuclear oxidation along with ethylation has also been employed in the study of the constitution of tambulin.[22]

(*b*) *Anthoxanthin glycosides.*—The application of this method of nuclear oxidation to the study of glycosides can be illustrated using gossypin and hibiscitrin. The former is 8-mono-glucoside of gossypetin (XLVII) and belongs to an unusual type. This conclusion was first arrived at from a consideration of its properties and reactions.[29] When fully methylated and the product hydrolysed a partial methyl ether with only one hydroxyl left out was obtained. It did not undergo fission with alkali satisfactorily; but veratric acid could be isolated as one of the products and this indicated that the free hydroxyl was in the benzopyrone part. The location of the hydroxyl in the 8-position (XLVIII) was first established by eliminating other possibilities using synthetic samples. This was supported by the oxidative demethylation[30] of this partial methyl ether yielding flavoquinone (XLIX) which could be reduced to the flavoquinol (L). This flavoquinol could be readily prepared, as already mentioned by the persulphate oxidation of tetramethyl-quercetin.[7] The conclusive stage was the ethylation of the partial methyl ether (XLVIII). The mixed ether (LI) not only underwent smooth alkali fission, but it could be easily synthesised by the stepwise ethylation and methylation of the flavoquinol (L) thus fixing the position of the ethoxyl and hence of the original glucose group unequivocally in the 8-position.



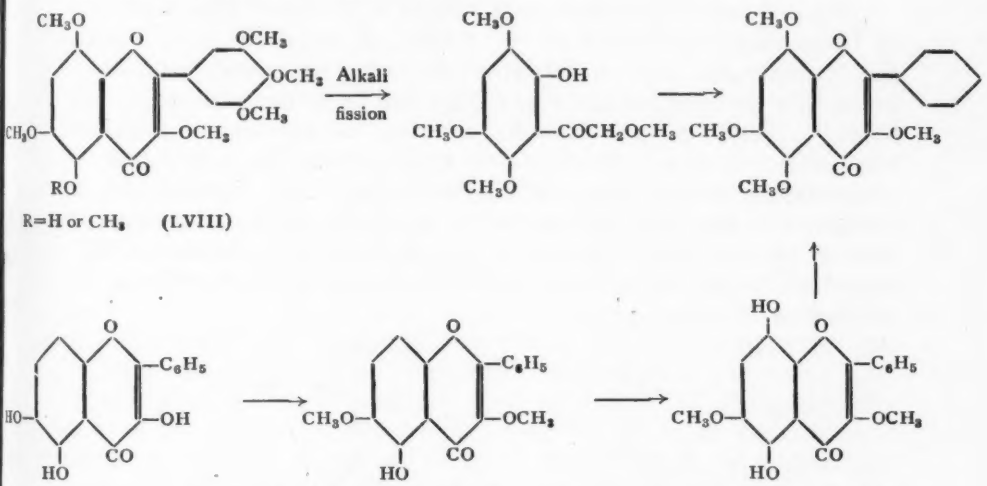
Hibiscitrin[31] is a monoglucoside of hibiscetin and belongs to a different type. On methylation and hydrolysis it yielded a hexa-methyl ether having one free hydroxyl group. Here again alkali fission yielded only the acid part as trimethyl gallic acid; the free hydroxyl was therefore in the benzo-pyrone half of the molecule. From a consideration of the properties of the glucoside and the degradation product the free hydroxyl was located to be in the 3-position (LIII) and hence hibiscitrin was a 3-glucoside (LII). The other alternative positions were also eliminated by the synthesis of suitable reference compounds for comparison. The method of nuclear oxidation made this work considerably easy. Final confirmation was obtained by ethylating (LIII) and synthesising the mixed ether (LIV) as follows. This compound further underwent smooth degradation with alkali to yield a ketonic part which could be definitely identified.



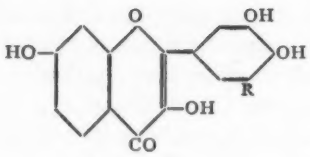
Quercetagitrin (LV) the monoglucoside of quercetagetin, forms a third typical example. After methylation and hydrolysis it yielded a pentamethyl ether of quercetagetin. Its properties and reactions and particularly the behaviour of the allyl ether indicated that the free hydroxyl was in the 7-position (LVI).[32] This has now been conclusively established by preparing its ethyl ether (LVII) and synthesising it in the manner[33] shown in page 14.

V. Gardenin

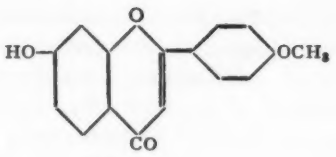
Gardenin[34] (LVIII, R = H) is a partial methyl ether of a flavonol belonging to a novel type not known before. That it has the 5:6:8-arrangement of substituent groups was arrived at by the elimination of all other possibilities. Definite confirmation of this constitution has recently been provided by Balakrishna and Seshadri[35] by synthetic experiments using nuclear oxidation as indicated below:



Flavones without the hydroxyl in the 7-position are rare in nature. Besides gardenin only primetin and 5-hydroxy flavone occur. They seem to result from the selective removal (reduction) of this hydroxyl at some stage of evolution. On the other hand fisetin (LIX, R = H) and robinetin (LIX, R = OH) are two flavonols devoid of the 5-hydroxyl group and pratol is a flavone (LX) of this type; again there are indications of the occurrence of 6:7:8-hydroxy-flavonols in the plant kingdom. Simple flavone which occurs as dust on various species of primula is an extreme case and lacks both these hydroxyl groups.



(LIX)

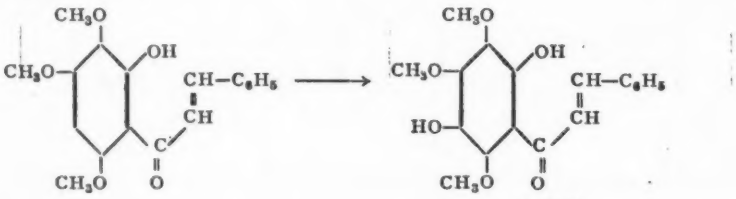


(LX)

VI. Pedicin and its Derivatives

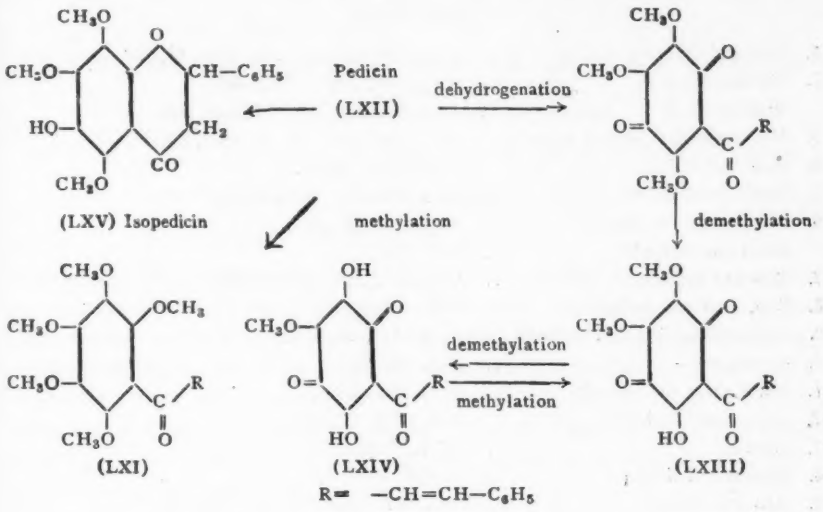
Mention has already been made that pedicin, pedicellin and their allies are examples of chalkones in which ring (A) is completely substituted. An interesting application has been made of nuclear oxidation in the recent study of this group of compounds. It is based on the easy formation by this method of *p*-dihydroxy chalkones which are otherwise not easily accessible.

The main crystalline components isolated by Siddiqui[36] from the leaves of Didymocarpus pedicellata are (1) pedicin, (2) isopedicin, (3) pedicellin and (4) pedicinin. The constitution of pedicellin was readily established as the fully methoxylated chalkone (LXI)[14] and its synthesis carried out by Baker.[37] There was some difficulty regarding the structure of pedicinin because that of pedicin was not correctly given; Sharma and Siddiqui[14] considered the latter to be an ortho-dihydroxy compound. From biogenetic considerations and from its reactions it appeared to us that this required revision and that pedicin should be a paradihydroxy compound (LXII). It has been shown to be so[15] and the new constitution has been confirmed by synthesis as follows:



(LXII)

The correct constitution of pedicin has thrown fresh light on the formula of pedicinin (LXIV) and on the biogenesis of the various compounds including methyl-pedicinin (LXIII) which has also been isolated from the leaves in this laboratory. Pedicin (LXII) which is a major component of the leaves, is considered to be the primary member formed according to the above synthetic process. The evolution of the others is indicated in the scheme given below and all the stages have been proved experimentally.



SUMMARY

The results contained in the recent publications from this laboratory on the subject of nuclear oxidation in the flavones and related compounds are summed up. Originally the main interest was in the theory of biogenesis of anthoxanthins; the bearing of the results on the evolution of the various types of flavones and flavonols is therefore discussed in detail. This study has led to the development of considerably simplified methods of synthesis of all the naturally occurring substances with three and four hydroxyl groups in ring A and of the special though simpler compounds like primetin. The application of this oxidation method along with ethylation for the establishment of the structure of partial methyl ethers as well as glycosides is illustrated by a number of typical examples. Special mention is made of the interesting and novel cases like gardenin and pedicin.

Note added in proof. In the above discussion of the persulphate oxidation and of the applicability of the results to the biogenesis of anthoxanthins, the benzopyrone part alone has been considered in detail. This is because the outcome of laboratory experiments regarding the side phenyl nucleus continued to be inconclusive. However, since submitting this paper for publication more definite results have been obtained and they will be published in a forthcoming paper.

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CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part V. Constitution of Auranetin

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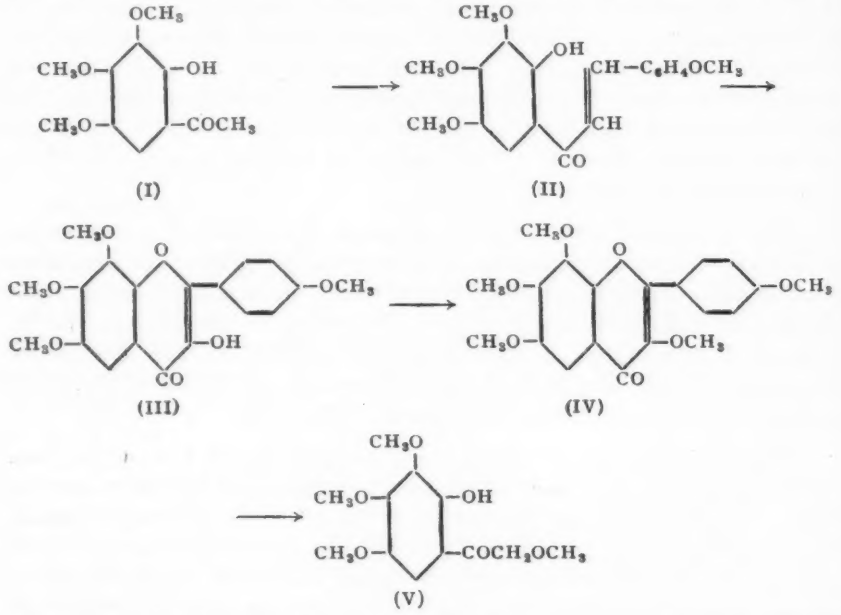
Received July 1, 1948

In an earlier paper (Part III[1]) was reported the isolation of a new compound in a small yield from the loose peels of kamala oranges, a local variety of *Citrus aurantium*. It was a fully methylated flavone like tangeretin and nobiletin and appeared to be a new entity found in the Citrus. It was named 'aurantin' based on its natural occurrence but it was realised later that this name had already been given to another substance isolated from the fungus *Oospora aurantia* (Cooke).[2] The name of the citrus product is now therefore changed to 'auranetin'.

The progress of work on the constitution of auranetin has been rather slow since, besides the difficulties of war years, the yield of the compound was very low and its purification was difficult. We examined similar fruits from other localities with the object of discovering a better source. So far this has been unsuccessful. The fruits from other places have not yielded any auranetin. Consequently a good portion of the earlier work had to depend on comparison with other known compounds.

The original sample of auranetin was not pure though it was crystalline. As the result of further work it has been possible to get colourless samples with a considerably higher melting point (139–40°). Its molecular formula is now definitely established as $C_{20}H_{20}O_7$ and it contains five methoxyl groups. Fission with alcoholic potash yielded anisic acid and a pale yellow ketone melting at 116–17° and having the formula $C_{12}H_{16}O_6$ with four methoxyl groups. It could not be studied further owing to lack of material. However the isolation of anisic acid narrowed down the possibilities. Auranetin was definitely different from tangeretin and pentamethyl herbacetin and the mixed melting points were lowered. The lower member of the nobiletin series (5 : 6 : 7 : 8 : 4′-pentamethoxy flavone) was then prepared.[3] It was found to melt at 150-51°. It was therefore clear that auranetin was a flavonol ether and the fairly smooth fission of the compound with alkali supported this opinion. Of the four possible structures for the flavonol pentamethyl ether, two, tangeretin and pentamethyl-herbacetin, were already

ruled out. The other two would have the 5:6:8 and 6:7:8 arrangement of methoxyl groups. The former though uncommon had recently been found in gardenin and 3:5:6:8:4′-pentamethoxy flavone[4] was therefore prepared for comparison. Its melting point was 142–43° which was very nearly that of auranetin; but a mixture of the two melted markedly lower. Thus by elimination auranetin should have the constitution of 3:6:7:8:4′-pentamethoxy flavone (IV). Flavonols with the 6:7:8-arrangement of hydroxyl or methoxyl groups have not so far been found to occur in nature. But the compound having the above constitution has been prepared a few years back by Bargellini and Oliverio[5] synthetically using the following steps.



The recorded properties of the pentamethyl ether, penta-hydroxy flavone and its acetate agreed with those of auranetin, norauranetin and its acetate. The melting points are compared in Table I. For purposes of direct comparison the compounds were synthesised. Since the original paper of Bargellini and Oliverio was not available at that time and only the abstract could be obtained, the methods of our preparation, being somewhat different, are briefly given. The agreement between the natural and synthetic samples is complete. Further the alkali fission of the synthetic pentamethyl ether yields besides anisic acid, 2-hydroxy-ω:3:4:5-tetramethoxy-acetophenone

(V) which is found to be identical with the ketone obtained from auranetin. Hence the identity of the two series, natural and synthetic, is established.

TABLE I

	Natural compounds	Synthetic compounds	
		Bargellini and Oliverio	Ours
1. Pentahydroxy compound ..	Above 360°	Above 360°	Above 360°
2. Methyl ether (Auranetin) ..	139–40°	141°	139–40°
3. Acetate ..	220–21°	216°	220–21°
4. Fission ketone ..	116–17°	..	116–17°

Thus in auranetin the citrus fruits have made another notable contribution to the chemistry of flavones. The American tangerine oranges provided the first fully methylated flavone, tangeretin[6] indicating the existence of a powerful methylation mechanism capable of attacking even the resistant 5-hydroxyl group. The Chinese mandarin oranges yielded nobiletin[7] which is not only a fully methylated flavone with six methoxyl groups, but has further a fully oxidised condensed benzene nucleus (5:6:7:8). The Indian kamala oranges have made the third contribution. Auranetin is another fully methylated compound and represents the so far unrepresented 6:7:8-combination of methoxyl groups. With this discovery the occurrence in nature of all the possible arrangements of three hydroxyl or methoxyl groups in the condensed benzene nucleus has been established. The most common are the 5:6:7 and 5:7:8 orientations and they are represented by a number of compounds. The 5:6:8-arrangement in which the 7-position is free is rare and it is represented only by the recently discovered gardenin. Similarly the 6:7:8-orientation of groups in which the 5-position is unsubstituted is equally rare and auranetin becomes the only known representative. Its evolution from the fundamental 5:7-hydroxy (quercetin) type should involve stages of oxidation of the positions 6 and 8 and reduction of the position 5 somewhat analogous to what has been suggested for gardenin.[8] In view of the considerations discussed in a recent publication[9] the following alternative seems to be the most probable.

$$5:7 \rightarrow 5:6:7 \rightarrow 5:6:7:8 \rightarrow 6:7:8$$

Though the removal of the 5-hydroxyl group may be possible at an earlier stage, oxidation of position 8 is best promoted by the presence of this group and it is therefore retained till the last stage in the above scheme.

Experimental

Isolation of Auranetin

The peels of the kamala oranges were sun dried and cut into small pieces and extracted with ligroin by heating on a water-bath for 10 hours; the yellow extract was poured out and the extraction repeated twice more. The extracts were combined and the solvent was distilled off under reduced pressure as competely as possible. The deep yellow oily residue was poured into an evaporating basin and the last traces of the solvent allowed to evaporate. The semi-solid product was triturated with cold methyl alcohol when most of the waxes and carotenoids remained undissolved and were filtered off. The methyl alcoholic solution was then evaporated and the remaining oily residue was dissolved in a small quantity of ether (1 volume) and diluted with four volumes of petroleum ether. A pale yellow crystalline solid began to separate in about a day; after a few days it was filtered and washed with a small quantity of petroleum ether to remove the adhering oil, and recrystallised from ether-petroleum ether mixture, when auranetin separated as almost colourless (very pale yellow) fine needles, m.p. 139–40°. (Found: in air-dried sample: C, 61·7; H, 6·0; loss on drying at 110° *in vacuo*, 4·2%; OCH_3, 40·2%; $C_{20}H_{20}O_7$, H_2O requires C, 61·5; H, 5·6; H_2O loss, 4·6%; OCH_3 for five OCH_3 groups, 39·7%. Found in the vacuum dried sample: C, 64·2; H, 5·8; OCH_3, 41·2; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4; OCH_3, 41·7%). The other properties and the reactions of auranetin were the same as described in detail in a previous paper.[1]

Nor-auranetin

Auranetin was demethylated with hydriodic acid as already described and nor-auranetin was recrystallised from a mixture of alcohol and acetic acid. It appeared as yellow rectangular rods under the microscope and on heating turned brown at about 300°, but did not melt below 360°. (Found in air dried sample: C, 56·5; H, 3·4; and loss on drying *in vacuo* at 120°, 5·1; $C_{15}H_{10}O_7$, H_2O requires C, 56·2; H, 3·7; loss on drying 5·6%. Found in the dried sample C, 59·3; H, 3·2; $C_{15}H_{10}O_7$ requires C, 59·6 and H, 3·3%).

The colour reactions of nor-auranetin in alkaline buffer solutions were already described. In 5% sodium carbonate solution, the compound dissolved with a deep red colour which was stable for 12 hours. A small quantity of a blue precipitate separated in half an hour.

Nor-auranetin was acetylated by boiling with acetic anhydride and sodium acetate for 2 hours. The product crystallised from ethyl acetate-petroleum ether mixture as colourless needles melting at 220-21°. (Found: C, 58·3; H, 4·3; $C_{25}H_{20}O_{12}$ requires C, 58·6 and H, 3·9%.)

Fission of Auranetin

Auranetin (1 g.) was dissolved in absolute alcoholic potash (2 g. in 25 c.c.) and the solution refluxed for 6 hours on a water-bath. At the end of the period, the alcohol was removed under reduced pressure, water added and the alkaline solution acidified. The mixture was extracted with ether and the ether extract washed successively with 5% sodium bicarbonate and 5% sodium hydroxide. Each of the solutions was acidified, extracted with ether, the extract dried over anhydrous sodium sulphate and the solvent evaporated. From the bicarbonate solution was thus obtained anisic acid, its melting point being undepressed on admixture with an authentic specimen. The sodium hydroxide extract gave a pale yellow compound (ketone) which after recrystallisation from alcohol formed pale yellow rectangular prisms and melted at 116–17°. It gave a brown colour with alcoholic ferric chloride. (Found: OCH_3, 45·6; $C_{12}H_{16}O_6$, H_2O requires OCH_3, 45·2%.)

2-*Hydroxy*-3 : 4 : 5 : 4′-*tetramethoxy-chalkone*[5] (*II*)

2-Hydroxy-3 : 4 : 5-trimethoxy acetophenone[10] (I) (1 g.) and anisaldehyde (5 c.c.) were dissolved in alcohol (20 c.c.) and to the solution was added aqueous sodium hydroxide (10 g. in 10 c.c. of water) in small quantities while cooling in ice. The flask was then corked air-tight and left for 2 days with occasional shaking. The deep-red solution slowly solidified; water was then added and the solution extracted with ether to remove the unreacted aldehyde. It was acidified and again extracted with ether. The ether extract was washed with sodium bicarbonate solution to remove anisic acid, dried over anhydrous sodium sulphate and the solvent removed. A yellow oil was obtained which turned into a bright yellow crystalline solid on leaving in the refrigerator. It crystallised from alcohol as deep yellow rectangular plates, melting at 111–12°. (Bargellini and Oliverio give the melting point as 110°.)

3-*Hydroxy*-6 : 7 : 8 : 4 -*tetramethoxy flavone*[5] (III)

The above chalkone (1 g.) was dissolved in rectified spirit (25 c.c.) and aqueous sodium hydroxide (2N, 50 c.c.). To the red solution was added hydrogen peroxide (100 vols. 10 c.c.) in small quantities with cooling under the tap and vigorous shaking. A yellow solid separated during the preliminary stages which later went into the solution with a deep yellow colour. The excess of hydrogen peroxide was decomposed by heating on a water-bath and then the alcohol evaporated off. On cooling the remaining solution and acidifying it, the flavonol separated as a brown solid. Recrystallisation from rectified spirit yielded it as yellow rods which melted at 186-7°. Yield 0·4 g. (Bargellini and Oliverio record the m.p. as 187°.)

3:6:7:8:4′-*Pentamethoxy flavone*[5] (*IV*).

The 3-hydroxy compound (III) was methylated with dimethyl sulphate and freshly ignited potassium carbonate in dry acetone solution by refluxing on a water-bath for 10 hours. The acetone was distilled off, water added to the residue and the aqueous solution extracted with ether. On evaporating the ether solution a colourless solid remained which crystallised from alcohol as very pale yellow needles melting at 139–40°. Mixed melting point with the natural sample of auranetin was undepressed. (Bargellin and Oliverio[5] give the melting point of the pentamethoxy flavone as 141°.)

3:6:7:8:4′-*Pentahydroxy flavone*.[5]

The pentamethoxy flavone (0·5 g.) was dissolved in acetic anhydride (5 c.c.) and to the solution was added hydriodic acid (5 c.c. of 1·7 d.) with cooling. The mixture was gently boiled for half an hour, cooled and diluted with water saturated with sulphur dioxide. The precipitated deep yellow solid was filtered and thoroughly washed with aqueous sulphur dioxide. It was dried and recrystallised from acetic acid when it was obtained as bright yellow rectangular plates. The compound turned brown at about 300°, but did not melt below 360°. (Bargellini and Oliverio also recorded the same property).

It was identical with nor-auranetin in all its properties and colour reactions, including those given by alkaline buffer solutions. Its acetate crystallised from absolute alcohol as colourless needles melting at 220–21°. It did not depress the melting point of the acetate of nor-auranetin. (Bargellini and Oliverio give the melting point of the acetate as 216°.)

The above pentamethoxy flavone was subjected to alkaline hydrolysis as in the case of auranetin. The products were anisic acid and the 2-hydroxy-ω:3:4:5-tetramethoxy acetophenone (V) melting at 116–17°; the melting point was not depressed by admixture with the ketone obtained from auranetin. (Found: C, 52·4; H, 6·8; Loss on drying *in vacuo* at 100°, 6·9; $C_{12}H_{16}O_6$, H_2O requires C, 52·6; and H, 6·6; H_2O loss 6·6%.)

Summary

Auranetin has been obtained pure. It is a colourless solid melting at 139–40° and is a pentamethoxy flavone. By alkali fission it yields anisic acid and a ketone containing four methoxyl groups. Direct comparison with compounds belonging to the types already known to occur in nature showed that it is quite novel and should belong to 6:7:8-methoxy type. This was confirmed by the preparation of 3:6:7:8-4′-pentamethoxy flavone and its derivatives and direct comparison. The ketone obtained

by the fission of the synthetic flavone is also identical with the one derived from auranetin. The contribution of citrus fruits to flavone chemistry and the biogenesis of the auranetin group are discussed.

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DIELECTRIC ANISOTROPY OF ROCKS

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Received June 24, 1948

(Communicatvd by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

Physical properties of rocks have assumed an importance in view of the recent developments in geophysical prospecting. Many of the properties have been widely studied, but generally without reference to the direction. Recently, Prasadarao[1] showed that there is anisotropy in the elastic behaviour of rocks. The ultrasonic velocity and the effective elastic constant have been found to be different in different directions. Koenigsberger[2] previously established experimentally that rock formations are in many cases not isotropic in their resistivity characteristics, and that differences as high as 20% may be observed in the values of some cleaved rocks in which determinations are made in directions parallel and perpendicular to the cleavage plane. Similar work on dielectric constants of rocks does not seem to have been reported. The author has accordingly undertaken a study of the same.

2. Experimental

The rock sections used in this investigation are the same as those employed by Prasadarao.[1] Jubbalpore marble (white), Hyderabad marble (grey), Rajaputana marble (pink), Bhima limestone, Kurnool limestone, Palnad limestone are the sedimentary types of rocks used. Keratophyre (Snowden, North Wales), norite (Kondapalle), chloritised dolerite (Hyderabad), leptynite (Kondavidu), eclogite (Scotland), Deccan trap (Rutlam), granite (Kondavidu), and pink coloured granite (Hyderabad) are the igneous types used. A full description of these rocks can be found in the communication referred to above.

Three mutually perpendicular sections are taken from each rock. One of them is parallel to the bedding plane or the cleavage plane. The other two are perpendicular to the above plane and also perpendicular to each other.

First of all the sections are dried at a temperature of 200° C. for four hours and the dielectric constants are then determined. Later, the sections are immersed in water for 15 minutes, taken out, and their surfaces wiped off.

They are left in a watch glass for over three days and the dielectric constants are again determined. When the sections are taken out, in the beginning they will have a larger moisture content but gradually they will lose some of the moisture and will finally retain a certain quantity, in equilibrium, depending upon the porosity of the section. So the dielectric constants of the rock sections are determined for this equilibrium moisture content. They may, to some extent, correspond to the dielectric constants of the rock *in situ* in different directions.

The method of determining the dielectric constants is the same as that developed and reported by the author[3] in an earlier communication. The determinations are made in the frequency range of 1 to 2 megacycles per second and at a temperature of 28° C.

3. Results

The dielectric constants of the sections in the dry condition and with equilibrium moisture content are given in the Table. K_1 is the dielectric constant perpendicular to the plane of easy breakage. K_2, K_3 are constants in two mutually perpendicular directions and contained in the plane of easy breakage. D_1, D_2, D_3 are the densities of the corresponding sections.

Specimen	Condition	D_1	K_1	D_2	K_2	D_3	K_3
Jubbulpore marble (white) ..	dry	2·85	7·7	2·84	7·7	..	..
	moist		7·9		7·9		
Hyderabad marble (grey) ..	dry	2·67	6·2	2·72	8·3	2·73	8·3
	moist		6·8		9·4		9·0
Rajaputana marble (pink) ..	dry	2·71	8·5	2·70	8·7	..	..
	moist		8·7		8·8		
Bhima limestone ..	dry	2·70	8·3	2·72	8·5	2·72	8·4
	moist		10·4		12·2		12·4
Kurnool limestone ..	dry	2·70	8·6	2·66	8·5	2·68	8·6
	moist		10·2		12·5		12·2
Palnad limestone ..	dry	2·69	7·8	2·67	7·8	2·68	7·9
	moist		10·6		12·0		12·1
Keratophyre ..	dry	2·63	5·7	2·58	5·5	..	..
	moist		5·9		5·9		
Norite ..	dry	3·07	10·9	3·08	12·0	..	..
	moist		11·3		12·7		
Chloritised dolerite ..	dry	3·04	8·3	3·01	8·2	..	..
	moist		9·7		10·7		
Leptynite ..	dry	2·68	6·1	2·66	6·1	2·68	6·3
	moist		6·4		7·1		7·1
Deccan trap ..	dry	2·86	11·2	2·88	12·0	..	..
	moist		13·0		15·5		
Eclogite ..	dry	3·37	12·7	3·26	9·7	3·25	9·3
	moist		17·0		14·1		13·6
Kondavidu granite ..	dry	2·62	5·9	2·62	5·9	2·61	5·8
	moist		8·4		8·7		8·7
Hyderabad gransite ..	dry	2·61	7·0	2·60	7·0	2·62	6·8
	moist		7·1		7·2		7·3

4. Discussion of Results

In the dry condition, the dielectric constants of the different sections of a rock, except in a few cases, are nearly the same. Small differences of 0·1 or 0·2 may be due to slight inhomogeneities in the rock.

In the case of norite, eclogite, and Deccan trap the dielectric constants are high and the differences of K_1, K_2, K_3 of the same rock in the dry condition are conisderable. Norite and Deccan trap are known to contain iron ore as a constituent. Eclogite contains the mineral rutile which in the crystalline state has the high dielectric constants of 89 and 173 in the perpendicular and parallel directions. The densities of the sections giving higher values are larger. In the case of eclogite, where the differences in the dielectric constants are very high, the density differences are marked. The differences of K_1, K_2, K_3 in these cases may be due to the non-homogeneous distribution of the iron or rutile content.

When the rock sections hold some moisture, the dielectric constants increase in value. This increase depends upon the amount of water held, and consequently the porosity. With the Jubbalpore and Rajaputana marbles the increases in the values are very small, indicating that the moisture those marbles can hold in equilibrium is small. The increase in the case of Hyderabad marble is more.

In the case of limestones, the values with the equilibrium moisture content are up to 50% more than the dry values. In the case of all limestones used, the values K_2, K_3 (moist) are nearly the same, whereas K_1 (moist) is different. So the increase in the dielectric constant with moisture perpendicular to the bedding plane is smaller than that parallel to the plane. This result is in consonance with Koenisberger's observation that the conductivity of the rock perpendicular to the bedding or cleavage plane is in some cases less than that parallel to the plane. Prasadarao found that the effective elastic constant perpendicular to the bedding plane is more than that parallel to the plane. So in the direction in which the elastic constant is less, the change of dielectric constant with moisture, and the conductivity are more.

In the case of the igneous rocks also the increase in the dielectric constant with moisture perpendicular to the cleavage plane is less than that parallel to the plane. The direction of the larger change in the dielectric constant with moisture happens to be the direction of the smaller elastic constant.

Prasadarao found that of all rocks, eclogite behaved elastically isotropic within 1%. But it happens to be the one which shows the maximum

variation in K_1, K_2, K_3 in the dry condition. That is likely to be due to the inhomogeneous distribution of rutile. The changes in the values of K_1, K_2, K_3 with moisture are nearly the same.

5. Summary

The dielectric constants of six sedimentary rocks and eight igneous rocks are determined. A directional study is made by cutting three mutually perpendicular sections, one of them being parallel to the plane of easy breakage. In the dry condition, the dielectric constants in different directions are found to be nearly the same for most cases. In the case of a few like eclogite, norite and deccan trap which have iron ores or rutile as constituents, there are differences in the values in different directions in the dry condition.

When the sections contain an equilibrium moisture content the values are found to be markedly different in different directions. The increase in the dielectric constant with moisture is found to be less perpendicular to the bedding or cleavage plane than that parallel to the plane.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam for his keen interest in the above investigation. His thanks are due to Mr. G. H. S. V. Prasadarao for lending the cut sections of the rocks.

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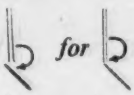
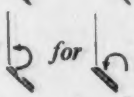
P. 379 in Structural Formula XIX, *read*  *for*

P. 379 in Structural Formula XX, *read*  *for*

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